

# Thermochemical Modeling of Oxide Glasses

## Introduction

Oxide glass materials have been in use for millennia, yet glass remains a highly enigmatic material. For example, the chemical thermodynamics of oxide melts, slags, and glasses have been difficult to model because of strong interactions between constituents, particularly with silica. Thus, unlike many metal alloys, simple solution models do not accurately reproduce the thermodynamic and phase relations in most oxide liquid systems. While lacking long-range order, oxide glass materials have very specific short-range/cluster periodicity that is a function of composition. Even oxide liquids exhibit short-range order and specific coordinations have been observed experimentally and computed using molecular dynamics.

An approach has been developed that is a fairly simple method for modeling these amorphous systems, and it has been termed the modified associate species model. The associate species approach is attractive because it (a) accurately represents the thermodynamic behavior of very complex chemical systems over wide temperature and composition ranges, (b) accurately predicts the activities of components in metastable equilibrium glass phases, (c) allows logical estimation of unknown thermodynamic values with an accuracy much greater than that required for predicting useful engineering limits on thermodynamic activities in solutions, and (d) is relatively easy for non-specialists in thermochemistry to understand and use. Ideally mixing associate species accurately represent the solution energies in which end member components exhibit attractive forces. The modification to the associate species model, hence the term “modified” associate species model, is the incorporation of positive solution model constants to represent any positive interaction energies in a solution. With these it is possible to accurately represent reported immiscibility in solution phases (e.g., liquid-liquid immiscibility common in many silica containing systems). The result is simple, well-behaved equations for free energies that can be confidently extrapolated and interpolated into unstudied temperature and composition ranges.

## Modified Associate Species Model

The associate species solution model uses intermediate “chemical species” with their corresponding thermodynamic data to represent the negative non-ideal mixing of the end-member components in a system. For example, liquid  $\text{NaAlO}_{2(l)}$  and  $\text{Na}_2\text{Al}_4\text{O}_7(l)$  species ideally mix with end-member  $\text{Na}_2\text{O}_{(l)}$  and  $\text{Al}_2\text{O}_{3(l)}$  to represent the liquid phase in the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$  binary system. While  $\text{NaAlO}_{2(l)}$  and  $\text{Na}_2\text{Al}_4\text{O}_7(l)$  may not exist as chemical entities that can be isolated and characterized, these species in the model can accurately represent the negative interaction energies that occur between sodium and aluminum in an oxide liquid solution.

All liquid associate species are written with formulae containing two non-oxygen atoms per mole, which equally weights each species with regard to its ideal mixing contribution. Thus the  $\text{Na}_2\text{Al}_4\text{O}_7(l)$  species noted above is actually  $\text{Na}_{2/3}\text{Al}_{4/3}\text{O}_{7/3}(l)$  or  $\text{Na}_2\text{Al}_4\text{O}_7:1/3(l)$  in the terminology used in the current work. This procedure was adopted during the optimization process when phase diagram information was being mathematically compared with thermodynamic data to obtain internally consistent sets of data for a given chemical system. It was determined that for all systems (aluminates, borates, silicates, aluminosilicates, etc.), the thermochemical data could more easily be

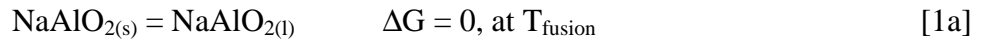
optimized when liquid associate species contained two non-oxygen atoms per species rather than one. This procedure influences the ideal mixing energy of the solution phase, but the implications of its use are not yet fully understood. However, for very stable liquid associate species, no ideal mixing energy (ideal mixing entropy) exists at the composition of that associate since one single associate species makes up the entire liquid solution at that composition.

Complex, multi-component system models are built up from the constituent binary and ternary systems. Binary and ternary constituent systems are modeled so that they accurately represent the experimentally determined phase equilibria. The various associates of these binaries and ternaries can then be included in a single ideal solution for a large number of constituent oxides, allowing equilibria to be easily computed and chemical activities derived. Where liquid immiscibilities exist in the binary and ternary systems such that some interaction terms are necessary to accommodate repulsive energetic relationships, these too can be used in fairly straightforward data-files. Unlike the modified quasi-chemical model, these interaction terms rarely require more than one or two terms, which include temperature dependencies. Fitting the phase diagram can be accomplished manually, obviating the need for sophisticated optimization routines.

### *Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> System*

A fundamental oxide system that is useful for illustrating the associate species approach is Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>. In using the associate species model to represent the thermodynamic properties of the liquid phase in the Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> binary oxide system, it was necessary to create an ideal liquid solution phase from end-member liquid components Na<sub>2</sub>O<sub>(l)</sub> and Al<sub>2</sub>O<sub>3(l)</sub>, and intermediates (associate species) NaAlO<sub>2(l)</sub> and Na<sub>2</sub>Al<sub>4</sub>O<sub>7(l)</sub>:1/3. While the utility of including the NaAlO<sub>2(l)</sub> associate species is apparent from its existence in the system as a crystalline phase, the additional use of Na<sub>2</sub>Al<sub>4</sub>O<sub>7(l)</sub>:1/3, which has no crystalline counterpart, was necessary in order to accurately reproduce the phase relations in the compositional region near Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub>=1:2. The initial thermochemical values for the NaAlO<sub>2(l)</sub> species that are used when starting the phase diagram/thermodynamic data optimization were derived from the crystalline phase, whereas the Na<sub>2</sub>Al<sub>4</sub>O<sub>7(l)</sub>:1/3 species initial values were estimated.

This initial free energy of formation of the associate species, NaAlO<sub>2(l)</sub>, is readily determined from considerations of the congruent melting reaction



where  $\Delta G$  is the total free energy change for the reaction and  $T_{\text{fusion}}$  is the melting temperature. The 298 K heat of formation,  $\Delta H_{f,298}$ , for NaAlO<sub>2(l)</sub> is the 298 K heat of formation for NaAlO<sub>2(s)</sub> plus the heat of fusion, and the 298 K entropy of the solid is similarly adjusted to give the liquid species entropy by adding the entropy of fusion. The result is that at  $T_{\text{fusion}}$

$$\Delta G_f(\text{NaAlO}_{2(s)}) = \Delta G_f^\circ(\text{NaAlO}_{2(s)}) = Y_{\text{Na}_2\text{O}}\Delta G_f(\text{Na}_2\text{O}_{(l)}) + Y_{\text{NaAlO}_2}\Delta G_f(\text{NaAlO}_{2(l)}) + Y_{\text{Na}_2\text{Al}_4\text{O}_7:1/3}\Delta G_f(\text{Na}_2\text{Al}_4\text{O}_7:1/3_{(l)}) + Y_{\text{Al}_2\text{O}_3}\Delta G_f(\text{Al}_2\text{O}_{3(l)}) \quad [1b]$$

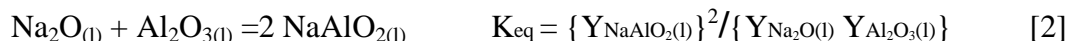
where  $\Delta G_f$  is the free energy of formation,  $\Delta G_f^\circ$  is the standard free energy of formation, and  $Y_i$  is the mole fraction of the liquid species  $i$ . The free energy and standard free

energy of formation of the solid are identical since the pure stoichiometric solid phase is defined as having unit activity,  $a=1$ . The same may not be true for the liquid phase in equilibrium with this solid since the liquid solution is composed of  $\text{Na}_2\text{O}_{(l)}$ ,  $\text{Al}_2\text{O}_{3(l)}$ ,  $\text{NaAlO}_{2(l)}$ , and  $\text{Na}_2\text{Al}_4\text{O}_{7(l)}$ :1/3 liquid species with the constraint that the liquid composition be identical to that of the solid phase composition at the congruent melting temperature. Since the liquid solution is ideal, the following type of equation holds for each liquid species.  $\text{NaAlO}_{2(l)}$  is used as an example, with  $Y_{\text{NaAlO}_2}$  being the mole fraction (activity) of this species in the liquid solution.

$$\Delta G_f(\text{NaAlO}_{2(l)}) = \Delta G_f^\circ(\text{NaAlO}_{2(l)}) + RT \ln Y_{\text{NaAlO}_2} \quad [1c]$$

Minimization of the total free energy determines the equilibrium state and the relative mole fractions of the species. Since the liquid phase is treated as an ideal solution, the activities of the liquid associate species are by definition equivalent to their mole fractions,  $a_i = Y_i$ , and these activities can be used to predict properties such as leaching behavior, corrosion reactions, and other important phenomena.

Chemical reactions and associated equilibrium constants can be used in determining the relative amounts of each species



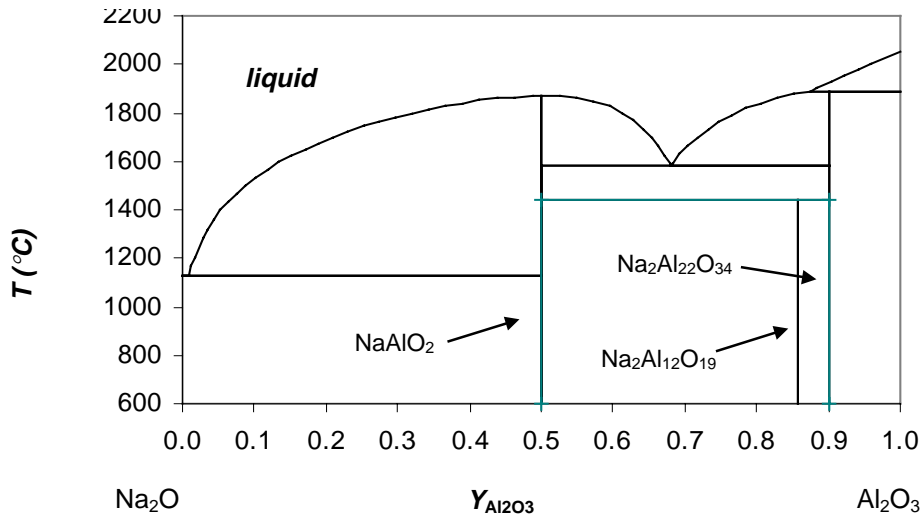
much as one would consider a homogeneous, equilibrium mixture of gaseous molecules. The activity values (mole fraction values) of these species at any given system composition could be inserted into equation [2] to calculate the value of  $K_{eq}$  at this temperature. Each system composition would result in the same value of  $K_{eq}$  at a given temperature for this reaction since for a given chemical reaction,  $K_{eq}$  is dependent only on temperature and not composition.

As noted above, equilibrium calculations that treat the end-member liquid species plus the associate species as an ideal solution allows complete description of the system. It is therefore possible to compute the phase relations and determine a phase diagram. ChemSage™ [14] was the primary tool for developing an assessed, internally consistent thermodynamic database, and for subsequent calculations of the equilibrium chemical behavior of the systems and drawing phase diagrams. The needed thermodynamic data are obtained from the literature, sources such as the assessed SGTE substance database, and estimates, and then simultaneously comparing and optimizing sets of phase equilibria and thermodynamic data.

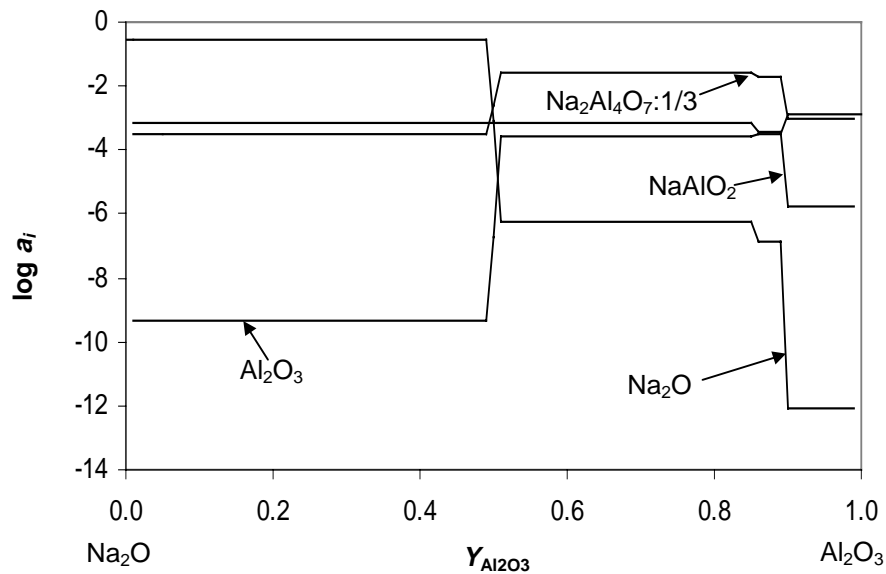
Typically, the thermodynamic values for the associate species are not sufficiently refined as to allow accurate reproduction of the phase diagram. Melting and other transition temperatures are very sensitive to thermodynamic values, and therefore small differences can result in significantly skewed phase equilibria. Thus, the initial thermodynamic properties of the associate species are modified to calculate phase relations that match those of the experimentally determined phase diagram. In the case of  $\text{NaAlO}_{2(l)}$ , as is often the general situation, the enthalpy of formation was slightly adjusted to fit the phase relations.

The chemical thermodynamic data set generated for the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$  system allowed the final computed phase diagram to be drawn by ChemSage™, as depicted in Figure 1a. The diagram compares exceedingly well with the experimentally reported phase relations. The software also computes the individual activities of the species, and for the liquid/glass species these are plotted in Figure 1b for 800°C. The calculations

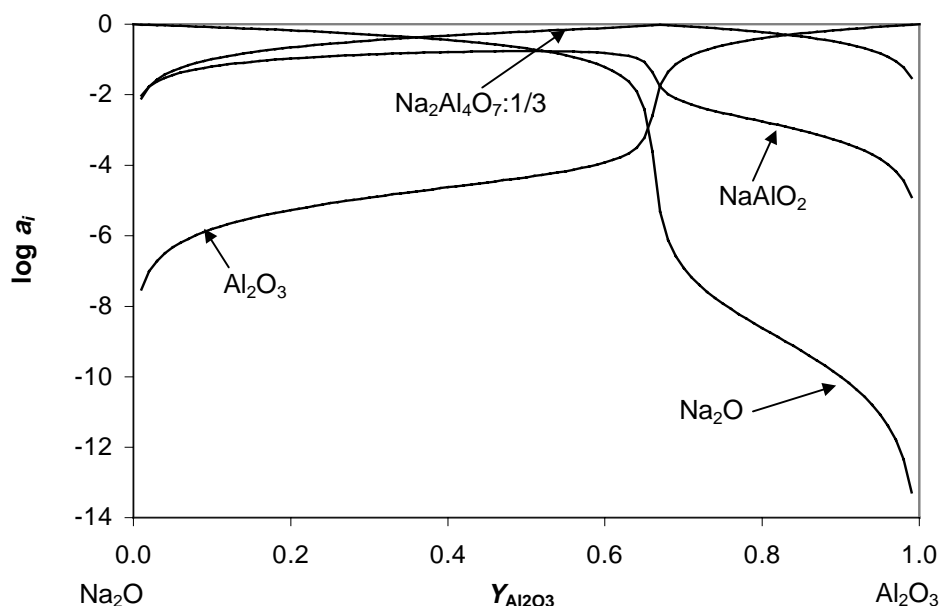
were performed such that the crystalline phases in the system were allowed to exist, thus the non-varying activities are the result of two-phase regions where all degrees of freedom are fixed. In contrast, calculations constrained such that no crystalline phases form, as would be the case for an under-cooled liquid forming a glass, the activities can be seen to vary smoothly (Figure 1c).



**Figure 1a.** Computed phase diagram for the  $\text{Na}_2\text{O}$ - $\text{Al}_2\text{O}_3$  system.



**Figure 1b.** Computed activities for the species in the associate species model for the glass phase in the  $\text{Na}_2\text{O}$ - $\text{Al}_2\text{O}_3$  system at  $800^\circ\text{C}$  where all crystalline phases are allowed to form. All lines should be horizontal or vertical as all degrees of freedom are fixed due to the presence of two phases over the entire compositional range.



**Figure 1c.** Computed activities for the species in the associate species model for the glass phase in the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$  system at  $800^\circ\text{C}$  where no crystalline phases are allowed to form. The curves vary continuously due to the presence of only the single glass phase.

The activities plotted in Figure 1c are illustrative of the relative stability, at least within the associate species model assumption, of the species in the glass. For this system the end member species,  $\text{Na}_2\text{O}_{(l)}$  and  $\text{Al}_2\text{O}_{3(l)}$ , only have high activities near the terminal compositions, and therefore are not controlling chemical behavior over much of the compositional region. The most important species is the associate  $\text{Na}_2\text{Al}_4\text{O}_{7(l)}:1/3$ , which has a high activity over almost the entire compositional range, approaching unity at  $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$  of 1:2, the species nominal composition that also coincides with the liquid eutectic composition between  $\text{NaAlO}_2$  and  $\text{NaAl}_9\text{O}_{14}$ . As noted earlier, this indicates that the glass exhibits a high degree of interaction between the component oxides, and is thus not well-represented by an ideal mixture of the end-members.

### *CaO-SiO<sub>2</sub> System*

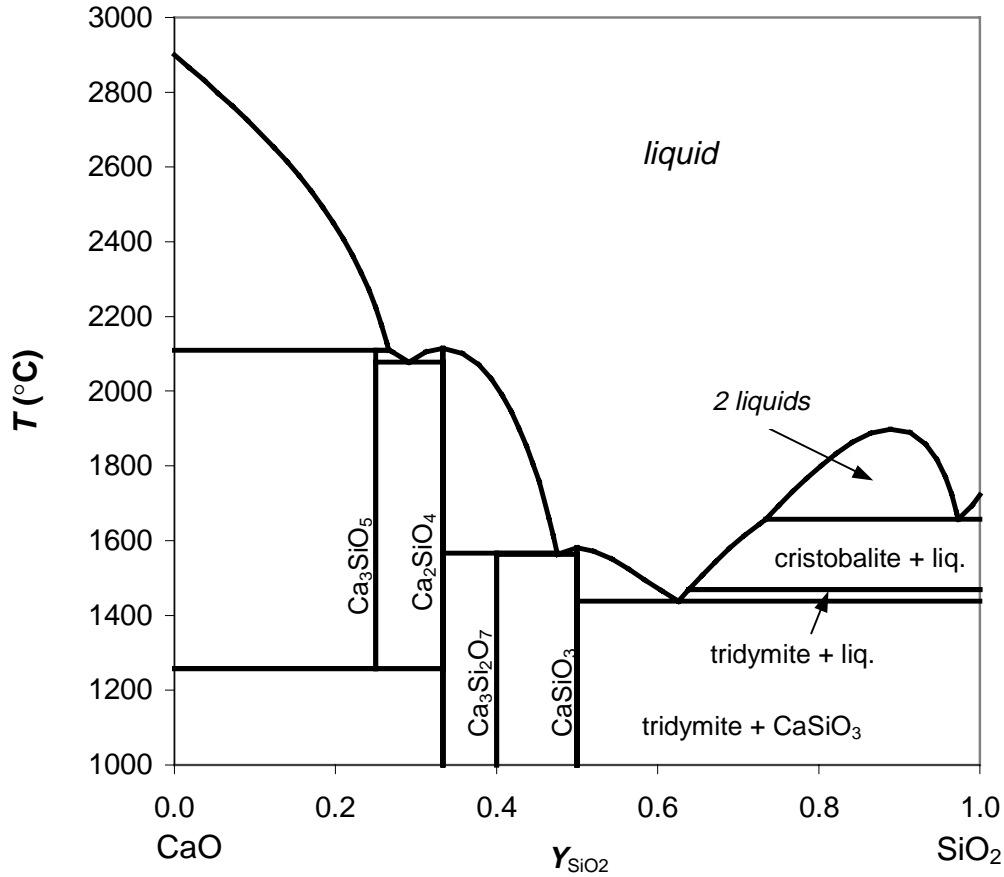
The  $\text{CaO}-\text{SiO}_2$  system is more complex to model and is a good example of treating liquid-liquid immiscibility using the modified associate species approach. As noted above, such immiscibility requires the solution to be treated as non-ideal, having positive interaction energies. The liquid for the  $\text{CaO}-\text{SiO}_2$  system contains the end member species  $\text{Ca}_2\text{O}_{2(l)}$  and  $\text{Si}_2\text{O}_{4(l)}$  plus the associates  $\text{Ca}_2\text{SiO}_{4(l)}:2/3$  (i.e.,  $\text{Ca}_{4/3}\text{Si}_{2/3}\text{O}_{8/3}$ ),  $\text{Ca}_3\text{SiO}_{5(l)}:1/2$  (i.e.,  $\text{Ca}_{3/2}\text{Si}_{1/2}\text{O}_{5/2}$ ), and  $\text{CaSiO}_{3(l)}$ . Again, the unusual stoichiometries are required to maintain 2 non-oxygen gram-atoms per mol of each species.

Figure 2a contains the computed phase diagram for the  $\text{CaO}-\text{SiO}_2$  system using parameters derived from the modified associate species model. The liquid-liquid

immiscibility region required the inclusion of non-ideal interaction terms between  $\text{CaSiO}_{3(l)}$  and  $\text{Si}_2\text{O}_{4(l)}$  such that the excess free energy,  $G_{\text{exs}}$ , is:

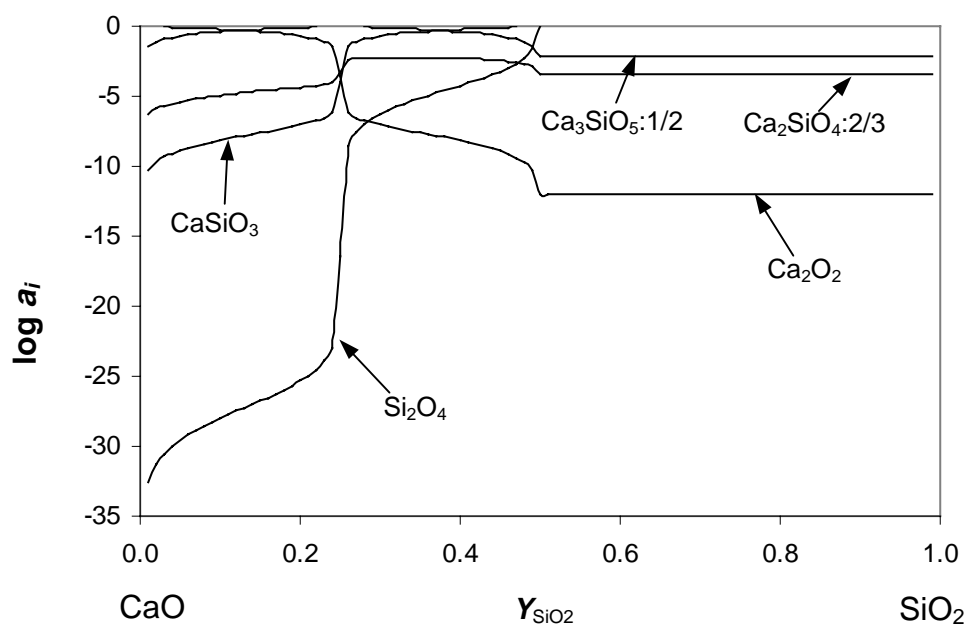
$$G_{\text{exs}} = X(1-X) \{ [141,000 - 65 \cdot T] + [(-10,000 - 10 \cdot T)(1-2X)] \} \quad (3)$$

where  $T$  is the absolute temperature (K). Given the great sensitivities of phase equilibria to thermodynamic values, the phase diagram is well-reproduced with this model.



**Figure 2a.** Computed phase diagram for the  $\text{CaO-SiO}_2$  system including representation of the two immiscible liquids region.

The chemical activities at  $800^\circ\text{C}$  of the species in the glass solution in the absence of crystalline phases were computed and are plotted in Figure 2b. At high calcia contents the species  $\text{Ca}_2\text{O}_{2(l)}$  and  $\text{Ca}_3\text{SiO}_{5(l):1/2}$  are dominant. In the high silica region the results of the positive interaction energies between  $\text{CaSiO}_3$  and  $\text{Si}_2\text{O}_4$  are apparent in their high activities, which approach unity. There are two glass phases present due to the immiscibility, thus constraining all the degrees of freedom and resulting in all activities being constant over this immiscible region.



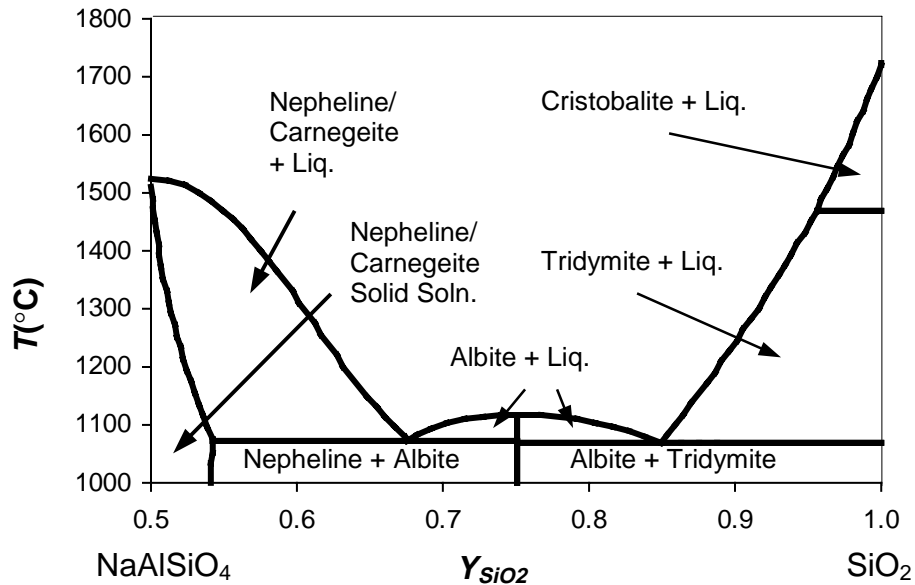
**Figure 2b.** Computed activities for the species in the associate species model for the glass phase in the CaO-SiO<sub>2</sub> system at 800°C where no crystalline phases are allowed to form. The curves vary continuously due to the presence of only the single glass phase at low silica content, but are invariant at high silica contents due to the presence of a second glass phase eliminating a degree of freedom.

#### *Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> System*

In developing the thermodynamic data file for the quaternary Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system, the thermodynamic and phase diagram data for six binary (Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O-SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, and B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>) and four ternary (Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>) subsystems were examined. In all cases, the complete set of thermochemical information for a system is refined and tested to give reasonable thermodynamic and phase diagram information over wide ranges of temperature and composition. Although a number of phases contain significant homogeneity ranges, in the current effort only mullite and nepheline were modeled as solid solutions over particular compositional ranges important to the proposed applications of the storage of nuclear waste in glass. Using the associate species approach for these crystalline solid solutions, successful models for the phases were developed. Nepheline was treated as an ideal solution of NaAlSiO<sub>4</sub>, NaAlSi<sub>2</sub>O<sub>6</sub>, and NaAlO<sub>2</sub>, and mullite was assumed to be composed of Al<sub>6</sub>B<sub>1.33</sub>O<sub>11</sub> and Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub>. The phases and species contained in the data file are listed in Table I and an example of a computed pseudobinary phase diagram that accurately represents experimental observations is seen in Figure 3.

**Table I.** Phases and species in the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$  system that constitute the solutions utilizing the modified associate species model. The fixed composition crystalline phases in this system are also listed.

Glass	Solution Phases	Crystalline	
$\text{Na}_2\text{O}$	Mullite:	$\text{Na}_2\text{O}$	$\text{Na}_2\text{B}_8\text{O}_{13}$
$\text{Al}_2\text{O}_3$	$\text{Al}_6\text{B}_{1.33}\text{O}_{11}$	$\text{Al}_2\text{O}_3$	$\text{NaB}_5\text{O}_8$
$\text{B}_2\text{O}_3$	$\text{Al}_6\text{Si}_2\text{O}_{13}$	$\text{B}_2\text{O}_3$	$\text{NaB}_9\text{O}_{14}$
$\text{Si}_2\text{O}_4$		$\text{SiO}_2$ (cris)	$\text{Na}_4\text{SiO}_4$
$\text{Al}_6\text{Si}_2\text{O}_{13}/4$		$\text{SiO}_2$ (trid)	$\text{Na}_6\text{Si}_2\text{O}_7$
$\text{NaAlO}_2$	Nepheline:	$\text{SiO}_2$ (quar)	$\text{Na}_2\text{SiO}_3$
$\text{Na}_2\text{Al}_4\text{O}_7/3$	$\text{NaAlSiO}_2$	$\text{NaAlO}_2$	$\text{Na}_2\text{Si}_2\text{O}_5$
$\text{Na}_4\text{B}_2\text{O}_5/3$	$\text{NaAlSi}_2\text{O}_6$	$\text{Na}_2\text{Al}_{12}\text{O}_{19}$	$\text{Na}_6\text{Si}_8\text{O}_{19}$
$\text{NaBO}_2$	$\text{NaAlO}_2$	$\text{NaAl}_9\text{O}_{14}$	$\text{NaAlSi}_3\text{O}_8$
$\text{Na}_2\text{B}_4\text{O}_7/3$		$\text{Na}_3\text{BO}_3$	
$\text{Na}_2\text{B}_8\text{O}_{13}/5$		$\text{Na}_4\text{B}_2\text{O}_5$	
$\text{Na}_4\text{SiO}_4/2/5$		$\text{NaBO}_2$	
$\text{Na}_2\text{SiO}_3/2/3$		$\text{Na}_2\text{B}_4\text{O}_7$	
$\text{Na}_2\text{Si}_2\text{O}_5/2$		$\text{NaB}_3\text{O}_5$	
$\text{NaAlSiO}_4/2/3$			
$\text{NaAlSi}_2\text{O}_6/1/2$			



**Figure 3** - Computed pseudobinary phase diagram over the compositional range from nepheline to silica.